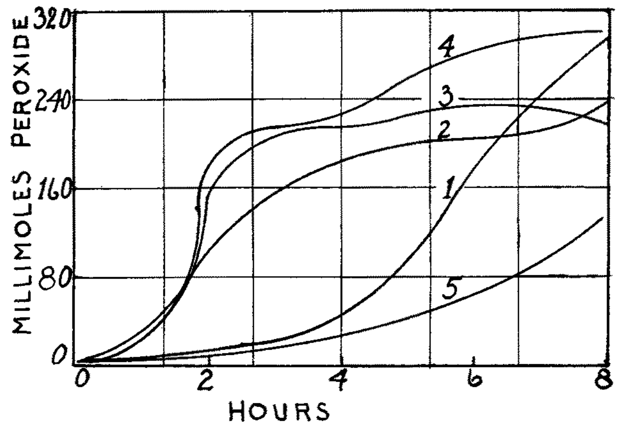
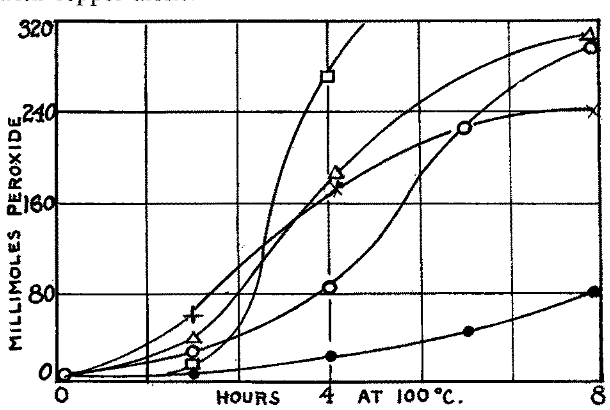


1. C. S. Oil (Control). 2. C. S. Oil 0.00025% Cu. 3. Control + 0.00025% Cu. + 0.01% Gossypol. 4. Control + 0.00025% Gossypol. 5. C. S. Oil + 0.01% Gossypol

Fig. 6. Aging Curve for C. S. Oil Containing Both Pro and Antioxidants Aged at 100° C.—200 W. Lamp at 15 Cm.

3 and 4. The initial oxidation rate is slightly less than with copper alone, but after two hours the rate of peroxide formation increases rapidly and the peroxide values remain higher than with copper alone for the next few hours. This is interpreted to indicate that gossypol inhibits the tendency of copper to break down the peroxides, thus giving higher peroxide titration values, although the actual rate of fat oxidation may be less than with copper alone.



O—Deod. C. S. Oil (Control). X—Control + 0.00025% Cu. △—Control + 0.00025% Cu. and 0.025% Stabilizer S-23. □—Control + 0.00025% Cu. and 0.1% Stabilizer S-23. ●—Control + 0.025% S-23

Fig. 7. Stability Tests on C. S. Oil Containing Both Pro and Antioxidants

The same experiment was repeated, replacing gossypol with a more effective anti-oxidant, and the results were similar throughout (Figure 7). After aging 3 hours, the sample containing copper plus the highest per cent of antioxidant (0.1%) showed the greatest apparent rate of peroxide formation. Moreover, 0.025 per cent antioxidant S 23 is not sufficient to offset the proöxidant effect of 0.00025 per cent copper, even in the early stages of oxidation, since the rate of peroxide formation in this case can be seen to be greater than the rate for the control throughout the test.

On the basis of these results and others of a similar character, irradiation, with or without the addition of small percentages of copper (in oil-soluble form), has become a regular feature of our work on anti-oxidants and fat stability. Copper is generally used only with highly stabilized oils or all-hydrogenated fats, in which the aging period cannot be shortened to a convenient value by irradiation alone. Other metals, especially manganese, can be substituted for copper, and the preferred manner of rendering these metals oil-soluble comprises the formation of soap by heating the metal acetate with fully hydrogenated cottonseed fatty acids in an atmosphere of hydrogen.

This work was conducted under the direction of L. C. Haskell, to whom grateful acknowledgment is made.

Summary

1. Purified gossypol has been shown to have marked antioxidant strength at low concentration.

2. The combined effect of added pro- and antioxidants on the rate of peroxide formation in cottonseed oil is shown graphically.

3. A modification of Wheeler's accelerated oxidation apparatus is described, which shortens the aging period by means of irradiation.

4. The methylene blue test has been checked against peroxide titration for the estimation of fat stability.

Literature Cited

1. E. P. Clark, Oil and Fat Industries, *6*, p. 15, (1929).
2. M. J. Cummings and H. A. Mattill, J. Nutrition, *3*, 4, p. 421, (1931).
3. H. A. Mattill, J. Biol. Chem., *90*, 1, p. 141, (1931).
4. Sidney Musher, U. S. 1,841,842, January 19, 1932.
5. R. C. Newton, Oil and Soap, *9*, 11, p. 247, (1932).
6. R. C. Newton and W. D. Richardson, Can. 323,764, June 28, 1932.
7. H. S. Olcott and H. A. Mattill, Ibid., *93*, p. 65, (1931).
8. H. D. Royce, Ind. Eng. Chem., Anal. Ed., (1933), in press.
9. F. C. Vibrans, Oil and Fat Industries, *8*, 6 p. 223, (1931).
10. J. Waddell and H. Steenbock, J. Biol. Chem., *80*, 2, p. 431, (1928).
11. D. H. Wheeler, Oil and Soap, *9*, 4, p. 89, (1932).

Cooking Cottonseed Meats Containing High Moisture

The ordinary method of cooking cottonseed meats containing a high moisture content is to increase the steam pressure in the jackets of the cookers and lengthen the cooking time. This results in producing a dark-colored cake, owing to the high temperature to which the meats in immediate contact with the hot walls of the cooker are raised occasioned by the inadequate stirring devices usually present. To obviate this difficulty, and produce a light-colored soft cake and an oil having a lower refining loss with a better color, the following method was used:

The meats containing 14 per cent to 17 per cent moisture were being cooked in a five-high stack cooker. A half-inch open steam pipe was carried into the meats in the top three sections of the cooker. Through this pipe live steam under 80 pounds pressure was fed directly into the meats, maintaining the steam pressure on the jackets which would be used for cooking meats containing a normal amount of moisture. The temperature of the meats in the top section was quickly raised to 210° F. Until the temperature of the meats reached 210° F., the meats were becoming wetter due to the condensed open steam. After the meats reached 210° F., the additional heat in the steam above 210° F. acted to evaporate the moisture in the meats. The open steam likewise acted to assist the agitation of the meats. The fan was run at a high speed to carry off the excess steam from the cooker. The temperature of the meats in the second and third sections from the top reached 215° F. and 220° F. respectively. The temperature in the bottom section was 228° F. The result was to produce a canary-colored soft cake having a lower extraction than had previously been obtained. The refining loss of the oil was reduced about 2 per cent due to the soapstock being firm and smooth compared with the soft soapstock that was normally obtained. In operating in this manner, there should be sufficient space above the meats in each section so that the open steam does not carry meats into the stack carrying the steam from the cooker. This plan can be varied to fit different moisture conditions. In general, the plan is to assist the evaporation of the excess moisture in the meats by means of open steam, either superheated or not.

R. H. Fash.

Gum Guaiac—A New Anti-Oxidant for Oils and Fats

By D. P. GRETTIE, Swift & Company, Chemical Laboratories

A New Antioxidant for Fats and Oils[1]

THE tendency of fats to undergo auto-oxidation, leading to physical and chemical changes, and to rancidity when they are exposed to atmospheric oxygen, has been a constant source of annoyance and loss to most industries in which fats are used or handled. A non-toxic antioxidant which prevents auto-oxidation in fats would have the function of preventing loss to the industries.

The most commonly accepted view concerning the mechanism of the auto-oxidation of fats postulates the intermediate formation of a highly reactive peroxide at the double bonds in unsaturated fatty acid radicals. This view was originally proposed by Engler and Wild[2], independently by Bach[3], and has been further elaborated upon by Milas[4] in his electronic interpretation.

A relatively large amount of this peroxide accumulates in a fat during auto-oxidation, before further reaction causes its break-down into other products, as is shown by the following tests:

1. By means of the oxygen absorption test, proposed by Greenbank and Holm[5], it can be shown that much oxygen is absorbed by fats during incubation, before the appearance of rancid odors which are due to the products of the decomposition of the peroxide.

2. The presence of peroxide in a fat after auto-oxidation has proceeded for some time can be demonstrated, quantitatively, by the peroxide oxygen test which was first proposed by Taffel and Revis[6], and further developed by others[7],[8]. This test is carried out by dissolving the fat in question in a solvent mixture, usually consisting of one volume of chloroform and two volumes of concentrated acetic acid, and adding a saturated solution of potassium iodide. The peroxide liberates its equivalent of iodine which is titrated with sodium thiosulfate.

3. The strong oxidizing effect of an auto-oxidized fat can be simply demonstrated by dissolving the fat in a suitable solvent, such as butyl alcohol, and adding phenylene-diamine which immediately darkens in color, showing that it has been oxidized.

It is evident from the above experiments that an auto-oxidized fat acts as a strong oxidizing agent under certain conditions.

The extensive works of Moreau and Dufraise, and co-authors, have demonstrated that certain compounds are enormously active in the prevention of auto-oxidation of oils and fats and certain other organic compounds. A review of this literature reveals that compounds acting as antioxidants prevent the accumulation of the highly reactive peroxide in the fat, and that rancidity under normal conditions does not develop until a considerable amount of peroxide has accumulated.

A large number of organic chemical compounds, all of which have reducing properties, act as antioxidants for fats. The ortho- and para-polyphenols, aromatic amines, and amino phenols are particularly active; so active, in fact, that .0001 of a per cent of pyrogallol or one part in 10,000,000 parts of dry fresh lard will have a noticeable effect in preventing the development of peroxide oxygen in the lard.

The author took up the study of anti-oxidants with the view in mind of making some practical use of anti-oxidants, either for edible or inedible fats. Several facts soon became manifest, however, that prevented immediate application:

1. Most anti-oxidants become ineffective when the fat to which the anti-oxidant has been added is washed with or exposed to water, particularly slightly alkaline water.

2. Many anti-oxidants have strong chemical odors and flavors.

3. Most anti-oxidants either have color or develop color shortly after addition to the fat—especially in the presence of weak alkali.

4. Much more of a given anti-oxidant is required for the protection of highly unsaturated vegetable oils than for the protection of lard or other animal fats.

5. Many of the known anti-oxidants are either poisonous or have unknown physiological effects.

The development of rancidity of fats after they have been incorporated into products of manufacture containing them is probably a greater source of annoyance than the development of rancidity in the fat itself during storage or marketing. Therefore, a successful anti-oxidant for edible fats must stabilize the fat after it is incorporated into products, such as crackers or other bakery products, that remain on the grocer's shelf during merchandising periods. After an examination of the known chemical anti-oxidants, we turned to some natural sources.

Pharmaceutical preparations of lard stabilized with gum benzoin have been known and prepared for many years. Gum benzoin is not sufficiently effective, however, to permit its use in food products, as appreciable quantities of gum benzoin impart an unpleasant, resinous odor to lard. We have tested, in addition to gum benzoin, many other natural gums and resins. Among those giving positive protection was gum guaiac, which proved successful not only in dry fats. but also in the presence of water, and in

[1]U. S. Patent 1,903,126 (Newton & Grettie).
[2]Engler, C., and Wild, W.—Ber. *30* 1669 (1897).
[3]Bach, A.—Compt. Rend. *124* 951 (1897).
[4]Milas, N. A.—J. Phys. Chemi. *33* 1204 (1929).
[5]Greenbank, G. R., and Holm, G. E.—Ind. & Eng. Chem. *17* 625 (1925).
[6]Taffel, A., and Revis, G.—J. Soc. Chem. Ind. 1931—87-91 T.
[7]Lea, C. H.—Proc. Royal Soc. *108 B:* 175-189 (1931).
[8]Wheeler, D. H.—Oil and Soap, *9* : 89 (1932).

Paper Read Before the American Oil Chemists' Society
May 12, 1933